

The Vaporization of B₂O₃(l) to B₂O₃(g) and B₂O₂(g) (Poster)

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The vaporization of B₂O₃ in a reducing environment leads to formation of both B₂O₃(g) and B₂O₂(g). While formation of B₂O₃(g) is well understood, many questions about the formation of B₂O₂(g) remain. Previous studies using B(s) + B₂O₃(l) have led to inconsistent thermodynamic data. In this study, it was found that after heating, B(s) and B₂O₃(l) appear to separate and variations in contact area likely led to the inconsistent vapor pressures of B₂O₂(g). To circumvent this problem, an activity of boron is fixed with a two-phase mixture of FeB and Fe₂B. Both second and third law enthalpies of formation were measured for B₂O₂(g) and B₂O₃(g). From these the enthalpies of formation at 298.15 K are calculated to be -479.9 ± 41.5 kJ/mol for B₂O₂(g) and -833.4 ± 13.1 kJ/mol for B₂O₃(g). Ab initio calculations to determine the enthalpies of formation of B₂O₂(g) and B₂O₃(g) were conducted using the W1BD composite method and show good agreement with the experimental values.

The Vaporization of $B_2O_3(l)$ to $B_2O_3(g)$ and $B_2O_3(g)$

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Vaporize $B_2O_3(l)$ in Reducing Environments

- Applications and need for thermodynamic data
 - Ceramic processing
 - Corrosion of high-temperature ceramics
- Two vaporization routes
 - $B_2O_3(l) = B_2O_3(g)$
 - $2/3 B \text{ (or other reductant)} + 2/3 B_2O_3(l) = B_2O_3(g)$
- Approach [1]
 - Ab initio study using quantum chemical composite methods
 - Knudsen effusion mass spectrometry (KEMS) [2]

Previous Studies

- Thermodynamics of $B_2O_3(g)$ well understood, reliable data available
- Questions on $2B(s) + 1/2 O_2(g) = B_2O_3(g)$; issues with B and $B_2O_3(l)$ rxn

Investigator/method and reaction	$\Delta_f H_{298.15}^\circ$ kJ/mol—2 nd Law	$\Delta_f H_{298.15}^\circ$ kJ/mol—3 rd Law	$\Delta_f H_{298.15}^\circ$
Inghram (KEMS) [3] $2/3 B + 2/3 B_2O_3(l) = B_2O_3(g)$	−509.4	−444.1	
Inghram (KEMS) [3] $2/3 B + 2/3 B_2O_3(g) = B_2O_3(g)$	−455.2	−458.7	
Scheer (Torsion) [4] $2/3 B + 2/3 B_2O_3(l) = B_2O_3(g)$	−428.6	−462.9	
Rentzepis et al. (Collection) [5] $C(s) + B_2O_3(l) = B_2O_3(g) + CO(g)$		−466.2	
Searcy and Myers [6] $2MgO(s) + 2B(s) = 2Mg(g) + B_2O_3(g)$		−458.9	
Nguyen et al. (ab initio) [7] $2B(g, \text{doublet}) + 2O(g, \text{triplet}) = B_2O_3(l)$			−457.7

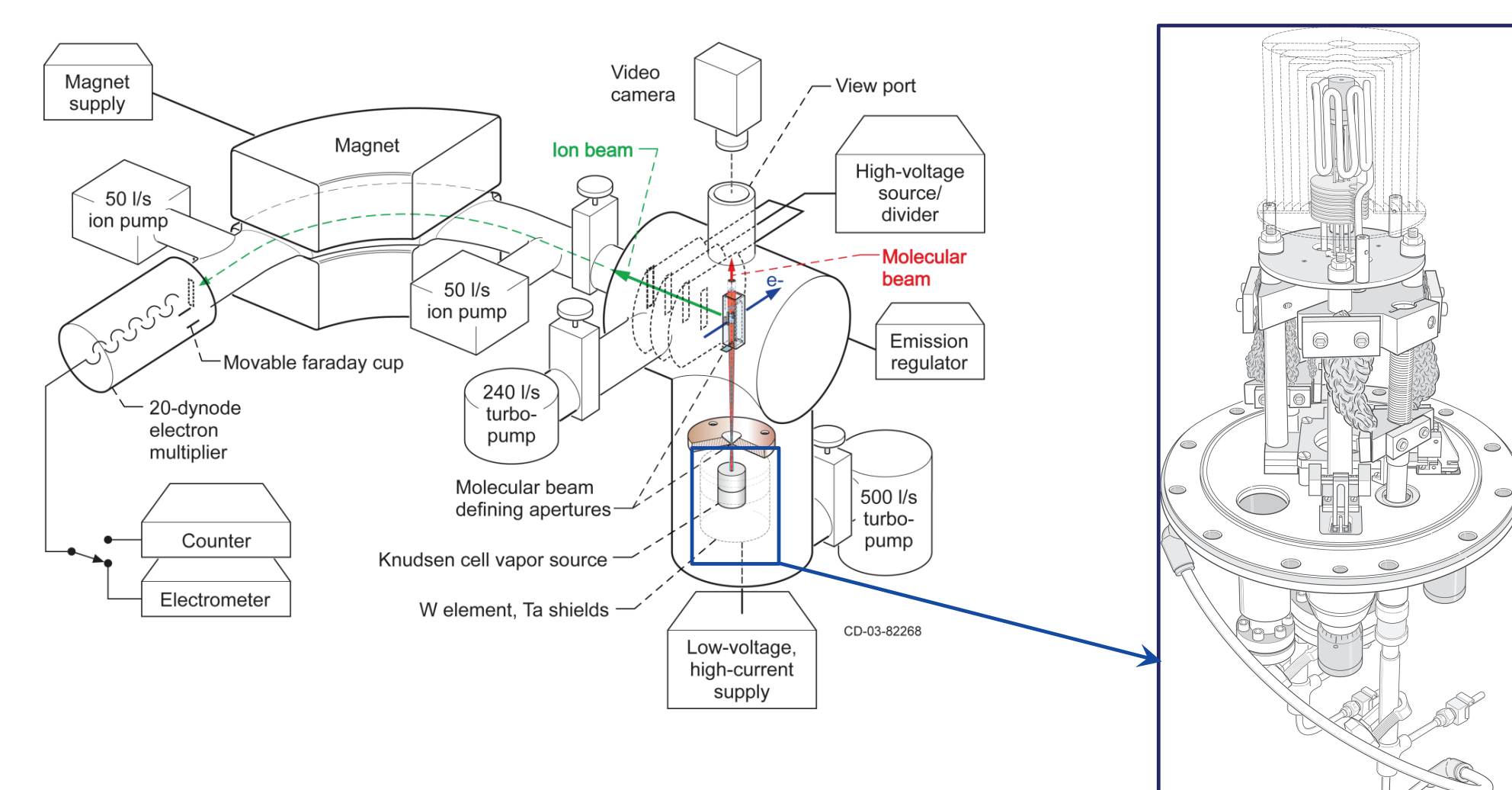
Theoretical Heats of Formation: Quantum Chemistry Composite Methods [8–12]

- Equilibrium geometry and frequencies computed at B3LYP/VTZ+1 level
 - Linear O–B–B–O shape for the $B_2O_3(g)$ and V shape for $B_2O_3(l)$
- W1BD Method, Gaussian Software [9,10]
 - Basis set: aug-cc-VnZ n = D,T, or Q
- Relativistic corrections/spin-orbit coupling effects included
- In the W1BD Modification of the W1 method, Brueckner Doubles used to simplify calculations
- Enthalpies of reaction determined from where all other reactants and products have known enthalpies of formation

Species/Reaction	W1BD Enthalpy/kJ mol ^{−1}	Nguyen <i>et al.</i> (7) Enthalpy/kJ mol ^{−1}
$B_2O_3(g)$		
$B_2O_3(l) = 2B(g, \text{doublet}) + 2O(g, \text{triplet})$	−479.9 ± 17.2	−457.7
$B_2O_3(g) + 6HF(g) = 2BF_3(g) + 2H_2O(g) + H_2(g)$	−456.7 ± 5.3	
$B_2O_3(g) + 6H_2(g) = 2BH_3(g) + 2H_2O(g) + H_2(g)$	−441.1 ± 14.7	
$B_2O_3(g)$		
$B_2O_3(l) = 2B(g, \text{doublet}) + 3O(g, \text{triplet})$	−857.4 ± 17.2	−830.1
$B_2O_3(g) + 6HF(g) = 2BF_3(g) + 3H_2O(g)$	−831.8 ± 5.3	
$B_2O_3(g) + 6H_2(g) = 2BH_3(g) + 3H_2O(g)$	−816.2 ± 14.8	

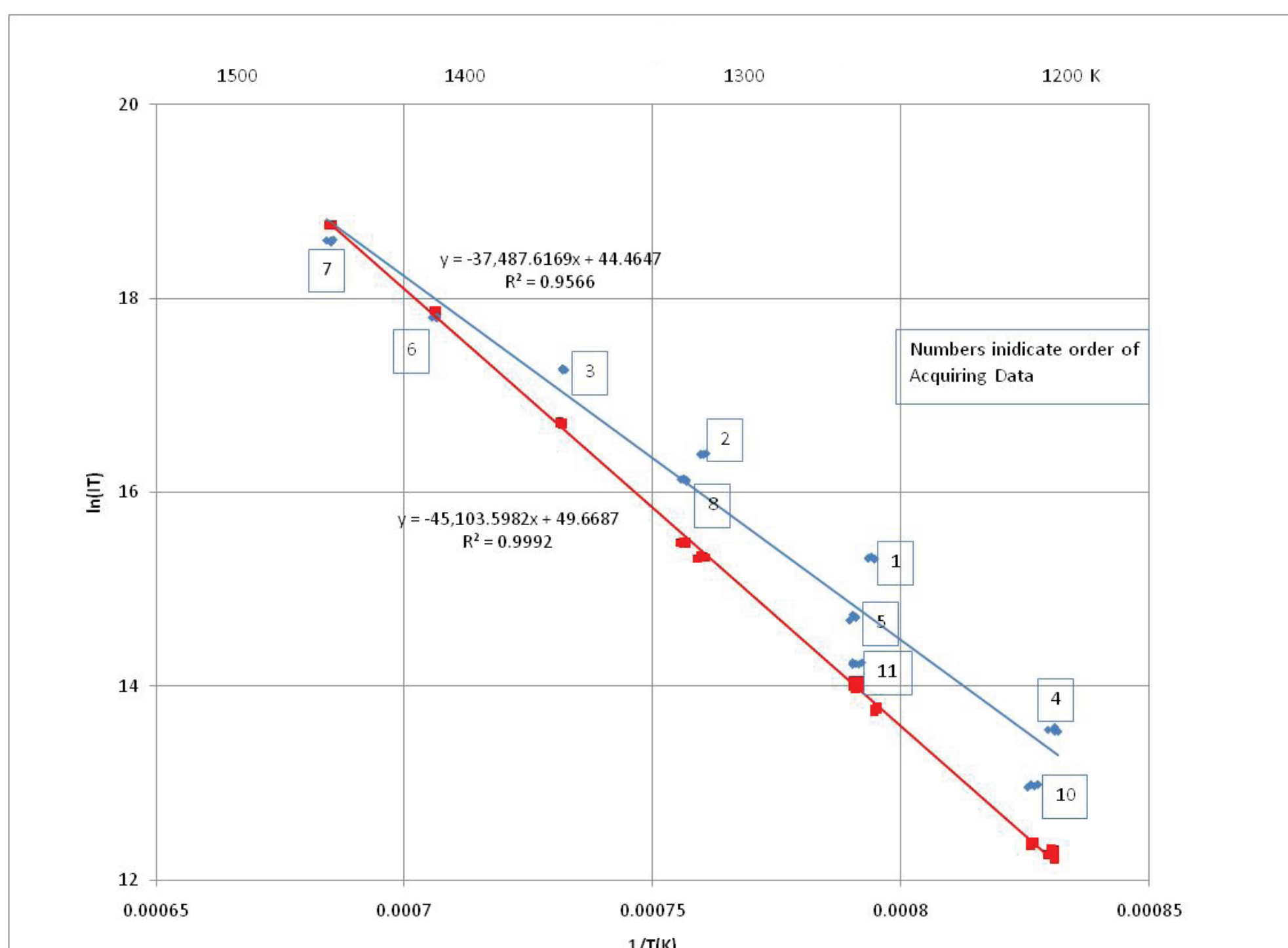
- Spin state is singlet, unless specified. Isogyric reactions (constant spin) preferred.

Glenn Research Center Knudsen Effusion Mass Spectrometer [2]

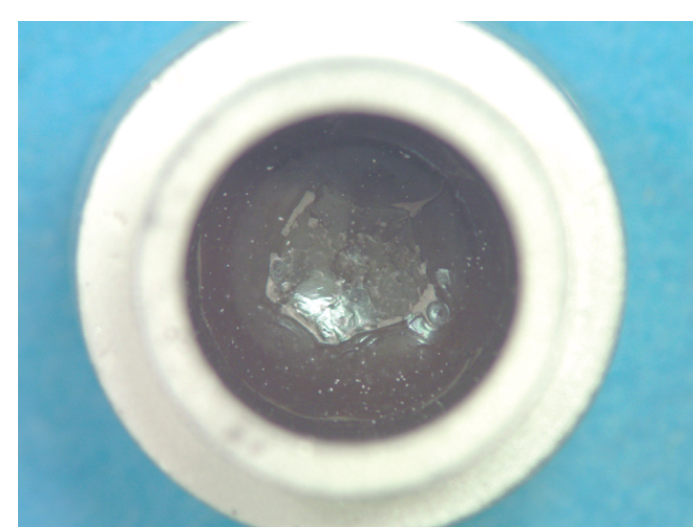


- Resistance heated cell
- Cross axis electron impact ionizer; 90° magnetic sector; and ion counting detector

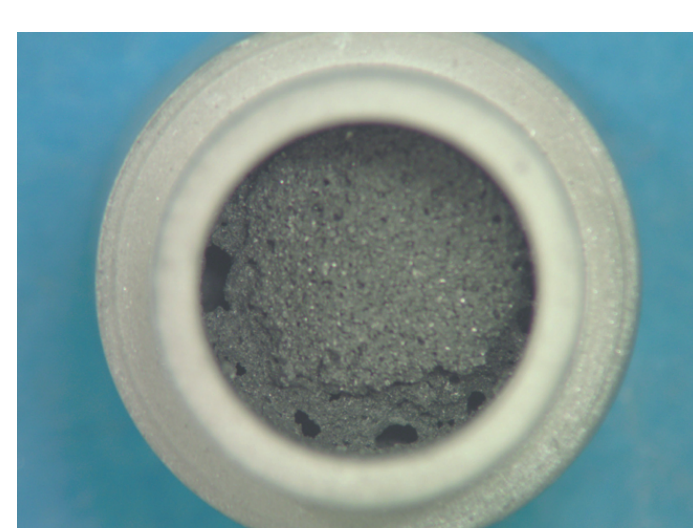
B + B_2O_3 in BN Single Cell 11-1, 2, 3-10



Selection of Proper Reductant for B_2O_3

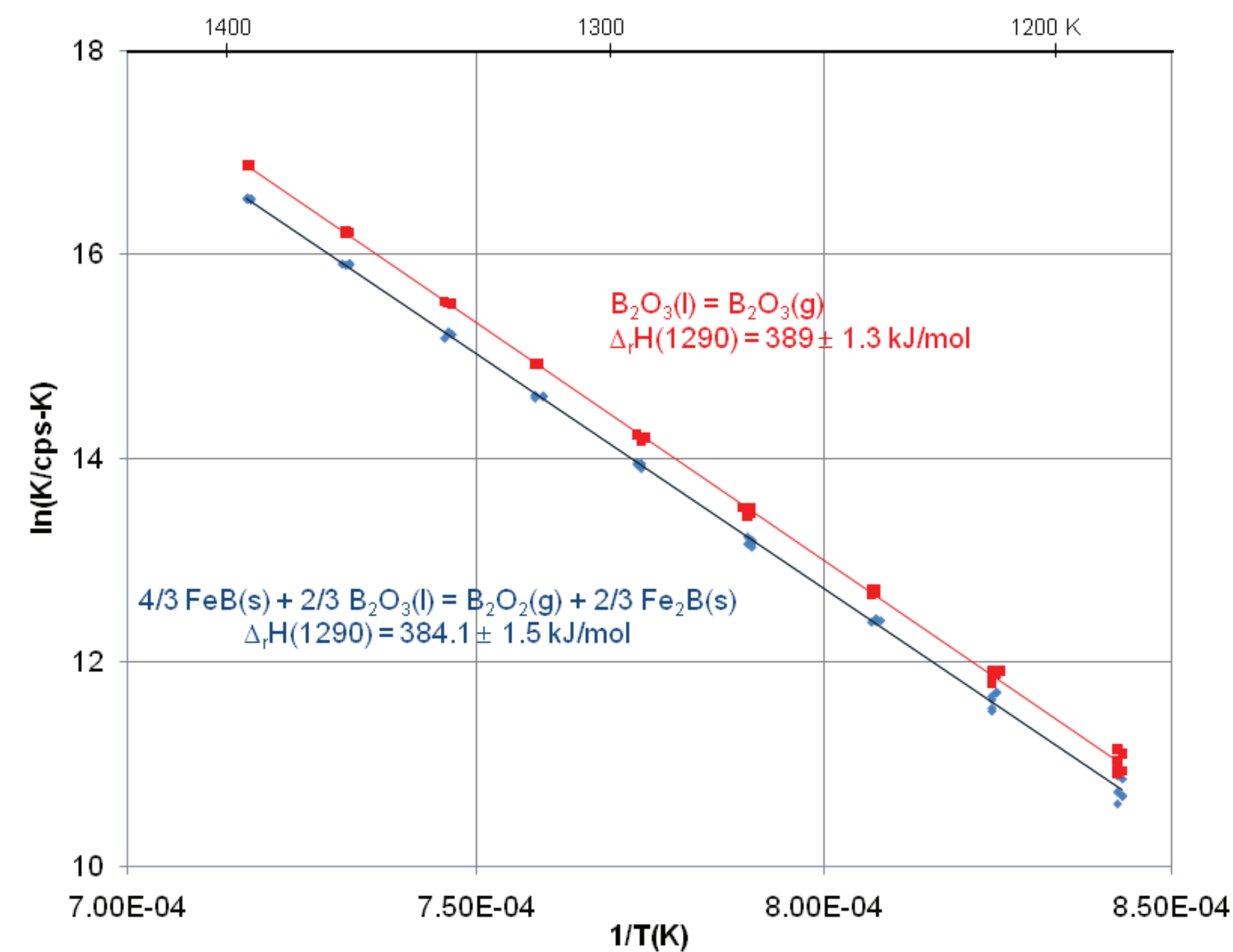


- B + B_2O_3
 - Used by other investigators
 - $B_2O_3(l)$ does not wet B
 - Changing contact area for $2/3 B + 2/3 B_2O_3(l) = B_2O_3(g)$
 - Led to lack of reproducible $B_2O_3(l)$ vapor pressures



- Use FeB/Fe₂B + B_2O_3
 - Two-phase mixture fixes B activity
 - No changes in mixture—contact area remains constant
 - $4/3 FeB + 2/3 B_2O_3(l) = B_2O_3(g) + 2/3 Fe_2B$
 - Gave reproducible vapor pressures

1:1:1 FeB:Fe₂B: B_2O_3 Mixture



Analysis of Data: Determine $\Delta_f H_{298.15}^\circ$

- 'Σ Plot' method [13,14]

$$\Delta \left\{ -(gef_{298.15}^\circ) \right\} - R \ln(I(i)T) = A + B/T$$

$$gef_{298.15}^\circ = (G_f^\circ - H_{298.15}^\circ)/T$$
 - Plot $\Delta \left\{ -(gef_{298.15}^\circ) \right\} - R \ln(I(i)T)$ vs $1/T$ Slope = $\Delta_f H_{298.15}^\circ$

- 'Third Law' method [15]
 - $T \left[\Delta \left\{ -(gef_{298.15}^\circ) \right\} - R \ln(K) \right] = \Delta_f H_{298.15}^\circ$
 - Obtain $\Delta_f H_{298.15}^\circ$ for each temperature

- Use experimental Gibbs Energy Functions (gef) [16]—preferred over calculated as determined from measured spectroscopic data

Analysis of Data: Determine $\Delta_f H_{298.15}^\circ$

- Use heats of formation of other compounds:
 - $4/3 FeB(s) + 2/3 B_2O_3(l) = B_2O_3(g) + 2/3 Fe_2B(s)$
 - $4/3 B(s) + O_2(g) = 2/3 B_2O_3(l)$ [16]
 - $4/3 Fe(s) + 4/3 B(s) = 4/3 FeB(s)$ [17]
 - $2/3 Fe_2B(s) = 4/3 Fe(s) + 2/3 B(s)$ [17]



- Total error must include error in each of these heats

Summary of Data for $\Delta_f H_{298.15}^\circ B_2O_2(g)$

Investigator and Technique	Data Points	Average Temperature	Enthalpy of Reaction			298.15 O ₂ (g) = B ₂ O ₃ (g)		Tables
			2 nd Law kJ/mol	2 nd Law kJ/mol	1 st Law kJ/mol	From 2 nd Law kJ/mol	From 1 st Law kJ/mol	
Inghram et al. KEMS [1] 2/3B + 2/3B ₂ O ₃ (l) = B ₂ O ₂ (g)	6	1400	302.5 ± 4.2	407.0 ± 7.2	391.5 ± 9.7*	-509.4	-444.1	
Inghram et al. KEMS [1] 2/3B + 2/3B ₂ O ₃ (g) = B ₂ O ₂ (g)	3	1410	103.4 ± 1.0	104.9 ± 1.1	101.4 ± 0.3	-453.2	-458.7	
Scheer—Torsion [4] 2/3B + 2/3B ₂ O ₃ (l) = B ₂ O ₂ (g)	14	1390	382.5 ± 7.2	326.2 ± 4.4	372.7 ± 2.0	-428.6	-462.9	
Rentzepis et al.—Collection [5] B ₂ O ₃ (l) + C = CO + 2B	5						-466.2 ± 6.5	
Searcy and Myers [6] 2MgO + 2B = 2Mg + B ₂ O ₃ (g)	1	1375					-458.9 ± 16.7	
JANAF [16]								-456.1 ± 8.4
NTNAP [18]								-457.728*
This Study Run 1 4/3 FeB(s) + 2/3 B ₂ O ₃ (l) = B ₂ O ₂ (g) + 2/3 Fe ₂ B	8	1284	363.8 ± 2.8	384.9 ± 2.9	411.0 ± 1.6	-498.0	-471.4	
This Study Run 1 4/3 FeB(s) + 2/3 B ₂ O ₃ (g) = B ₂ O ₂ (g) + 2/3 Fe ₂ B	8	1284	113.0 ± 2.1	115.6 ± 2.1	125.1 ± 0.8	-489.2	-479.7	
This Study Run 2 4/3 FeB(s) + 2/3 B ₂ O ₃ (l) = B ₂ O ₂ (g) + 2/3 Fe ₂ B	6	1280	376.7 ± 1.4	399.0 ± 1.5	413.0 ± 0.9	-484.0	-478.0	
This Study Run 2 4/3 FeB(s) + 2/3 B ₂ O ₃ (g) = B ₂ O ₂ (g) + 2/3 Fe ₂ B	6	1280	122.9 ± 1.8	125.6 ± 1.8	125.8 ± 0.5	-479.2	-478.0	
This Study Run 3 4/3 FeB(s) + 2/3 B ₂ O ₃ (l) = B ₂ O ₂ (g) + 2/3 Fe ₂ B	9	1290	384.0 ± 1.5	400.5 ± 1.5	414.0 ± 0.7	-477.5	-480.0	
This Study Run 3 4/3 FeB(s) + 2/3 B ₂ O ₃ (g) = B ₂ O ₂ (g) + 2/3 Fe ₂ B	9	1290	121.6 ± 1.7	123.7 ± 1.7	126.20 ± 0.6	-481.1	-478.6	

*Inghram et al. only converted three points to pressure and hence only three points were used for the 3rd Law enthalpy.
**Given class of accuracy is 6-F, which means an uncertainty is ±40 kJ/mol

Summary of Data for $\Delta_f H_{298.15}^\circ B_2O_3(g)$

Investigator	Number of Data Points	Average Temperature T	$B_2O_3(l) = B_2O_3(g)$			$2B(s) + 3/2 O_2(g) = B_2O_3(g)$		Tables
			2 nd Law	2 nd Law	3 rd Law	From 2 nd Law	From 3 rd Law	
Hildenbrand—Torsion [19]			302.5 ± 4.2	427.5	417.3	−525.9	−536.0	
Scheer—Torsion [20]	14	1500	364.9 ± 3.8	405.2 ± 3.9	424.2 ± 0.9	−484.2	−529.2	
Shuler et al.—mass spectrometry and weight loss [21]	14			412.1 ± 8.4	415.5 ± 0.1			
JANAF [16]							−536.0 ± 4.2	
NTNAP [18]							−535.383*	
This Study— B_2O_3 only	11	1320	380.8 ± 1.2	410.7 ± 1.3	429.5 ± 1.2	−442.6	−523.9	
This Study Run 1 $FeB/Fe_2B/B_2O_3$	8	1270	373.2 ± 1.7	401.7 ± 1.8	428.7 ± 1.7	−551.7	−524.7	
This Study Run 2 $FeB/Fe_2B/B_2O_3$	6	1225	380.8 ± 1.7	409.9 ± 1.7	430.3 ± 1.3	−543.5	−523.1	
This Study Run 3 $FeB/Fe_2B/B_2O_3$	9	1290	389.0 ± 1.3	417.9 ± 1.3	430.9 ± 0.6	−535.5	−522.5	

Conclusions

- Theoretical and experimental determination of heat of formation of $B_2O_2(g)$ and $B_2O_3(g)$
- Theoretical: Quantum chemistry composite method
- Experimental: Use Fe₂B/FeB mixture to set B activity, gave more reliable results than B alone
- For $B_2O_2(g)$ $\Delta_f H_{298.15}^\circ = -479.9 \pm 25.7$ kJ/mol
- For $B_2O_3(g)$ $\Delta_f H_{298.15}^\circ = -833.4 \pm 13.1$ kJ/mol

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